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MOLECULAR THEORY OF SOLUTIONS AND EXTRACTION OF METALS AND ACIDS BY ASSOCIATED REAGENTS

bу

Ye. V. Komarov



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### RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russiań	English	Russian	Énglish	Russian	English
sin	sin	sh	sinh	arc sh	$sinh_{-1}^{-1}$
cos	cos	ch	cosh	arc ch	cosh_1
tg	tan	th	tanh	arc th	$tanh_{-1}$
ctg	cot	cth	coth	arc cth	coth_1
sec	sec	sch	sech	arc sch	sech_1
cosec	csc	csch	csch	arc csch	csch

Russian	English
rot	curl
lg	log

<sup>\*</sup>ye initially, after vowels, and after ъ, ь; e elsewhere. When written as e in Russian, transliterate as ye or e.

# MÔLECULAR THEORY OF SOLUTIONS AND EXTRACTION OF METALS AND ACIDS BY ASSOCIATED REAGENTS

### Yē. V. Komārov

During the investigation of extraction of actinide and other elements and acids by such associated reagents as organophosphorous acids, the salts of amines and others, frequently dependences of the coefficients of distribution of substance on the concentration of the extracting reagent are observed which are very simple in overall nature. There is surprise in the fact that, for example, the extraction of nitric acid from an aqueous solution of nitrates of amines can be described within the framework of the simplest stoichiometric relationships without taking polymerization into account [1], without taking into account the strong deviation of the behavior of such solutions from the laws of behavior of ideal solutions. Just as incomprehensible (from the point of view of customary concepts) are the linear dependences (in logarithmic scale) of the coefficients of distribution of different metals on the concentration of reagent in the case of extraction by amines [2-8], monoalky1= and monoarylphosphoric acids [9-13].

Attempts at taking polymerization into account should unavoidably lead to consideration of the sum of reactions of the form

## i · M + A; Kis MiA,

where M = acid, salt or ion of the metal,  $A_r = r$ -mer of the reagent,  $K_{\dot{1}\dot{r}}$  - equilibrium constants of the corresponding reactions. In this case the expression for the coefficient of distribution M should include the following sum

$$\sum_{r,i}^{\infty} i \left[ \hat{a}_{\tilde{\mathbf{M}}} \right]^{t} \left[ \hat{\mathbf{A}}_{r} \right] \frac{\gamma_{r}}{\gamma_{\tilde{\mathbf{M}}_{i\hat{r}}}} K_{ir},$$

where  $a_{M}$  - activity of M in the aqueous phase,  $[A_{\hat{r}}]$  - concentration of  $\hat{r}$ -mer in the organic phase,  $\gamma_{M_{\hat{1}\hat{r}}}$  - activity coefficient of a complex of the composition  $M_{\hat{1}}A_{\hat{r}}$ ,  $\gamma_{\hat{r}}$  - coefficients of activity of the  $\hat{r}$ -mer of reagent A.

In order to describe exactly the concentration dependence of the coefficient of distribution of particles M, it is necessary to know, in addition to the variables Kin, the dependence on grossconcentration of the reagent of the content of different associates  $[A_r]$  and the variables  $\frac{\gamma_r}{\gamma_{M_r}}$ for the different complexes and associates. The selection of specific conditions for carrying out the experiment makes it possible at least to find the concentrations of  $[A_n]$  by independent methods of physicochemical analysis. The experimental determination of the coefficients of activity of individual associates and complexes is just as difficult (or even impossible) a problem as the determination of the absolute activities of the individual ions of the electrolyte. Therefore for the calculation of the variable we have no other route except théoretical calculation.

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Selection of the molecular-statistical model. Molecular theolies of associated solutions developed rapidly especially in the fifties. The successes in this area were reflected in a number of monographs and reviews [13-18]. In analyzing the dependences of thermodynamic functions on the composition of associated solu-

tions of different types, Rowlinson [14] came to the conclusion that the sign and magnitude of thermodynamic functions of mixing in systems with strong directed bonds between the molecules are determined mainly by the change in the number of such bonds during mixing of an associated liquid with other liquids. that out of the different variants of molecular theories of associated solutions that one should be selected, in which in the construction of the statistical sum of the molecular mixture in an evident form the formation of associates and solvates is taken into consideration [13, 19-21]. Since such a route takes into account the contributions from the change in internal energy and the orderliness of molecules in the system, then corrections for the effects of a second order of smallness, conditioned by the change in the molecular environment of associates and solvates with the change in the composition of the system, can be found on the basis of the theory of strictly regular solutions in a zero approximation [16].

The special features of the selected molecular-statistical model of a solution are reflected precisely in the following record-ing of the statistical sum of a molecular mixture

$$Z = g(N_{\mathrm{D}}, N_{\mathrm{T}}) \prod_{\mathrm{D}} \psi_{\mathrm{D}}^{N_{\mathrm{D}}} \cdot e^{-\frac{U(N_{\mathrm{D}}, N_{\mathrm{T}})}{kT}}, \tag{1}$$

where the indices  $\bar{D}$  and  $\bar{T}$  are the generalized symbols of the sort of all possible particles (including associates and solvates) in the system,  $N_D$  - number of particles of sort D,  $g(N_D, N_T)$  - number of configurations of the mixture,  $\psi_D$  - statistical sum based on the inner states of a particle of sort D,  $U(N_D, \bar{N}_T)$  - configuration energy of the system, depending on the number and class of contacts of all possible particles in the system.

The variable g can be calculated by using Guggenheim's formula [16], if the molecular complexes are either cyclic or noncyclic. In the case of particles of an arbitrary form a generalized Guggen-

heim formula should be used [22]. The variable  $\hat{U}$  can be calculated in the following manner.

A molecule of a given sort D in a general case has surface sectors which are not equivalent to each other in an energy respect. Assume  $\epsilon$  and  $\nu$  are generalized symbols of the class of contact sectors of the molecule, so that  $\epsilon$  can take specific values of a, b, c, etc., just as  $\nu$  (the second symbol is introduced for indicating the difference of classes of contact sectors)\*

\*Here the symbols developed by Barker are applicable [23].

The share of contact sectors of molecule D in class  $\epsilon$  is designated by the symbol  $V_{\xi}^D$  . Evidently 5

The variable  $\mathcal{U}_{\epsilon\nu}$  denotes the energy of the contact, formed by the contact sectors of classes  $\epsilon$  and  $\nu$  of particles of the same or different sorts. The overall number of all possible contacts will be equal to

$$Q = \frac{1}{2} z \sum_{\mathbf{D}} q_{\mathbf{D}} N_{\mathbf{D}}.$$

Here  $zq_{\vec{D}}$  - number of nearest neighbors of a molecule of sort  $\hat{D}$ ,  $\hat{z}$  - coordination number of the lattice.

The share of contact sectors of class  $\dot{\mathcal{E}}$  of all the particles in the solution will be equal to

$$V_{\epsilon} = \frac{\sum_{\mathbf{D}} q_{\mathbf{D}} \cdot V_{\epsilon}^{\mathbf{D}} N_{\mathbf{D}}}{\sum_{\mathbf{Q}} q_{\mathbf{D}} N_{\mathbf{D}}}.$$
 (2)

It is easy to show that the overall number of contacts of type ( $\mathcal{E}-\mathcal{V}$ ) will be equal to  $QV_{\mathcal{E}}V_{\mathcal{V}}$ , and their energy  $QV_{\mathcal{E}}V_{\mathcal{V}}\cdot U_{\mathcal{E}\mathcal{V}}$ .

The dependence of the configuration energy on composition of the solution will be expressed as:

$$U(N_{\tilde{\mathbf{D}}}, N_{\tilde{\mathbf{T}}}) = Q \sum_{\mathbf{s}, \mathbf{v}} V_{\mathbf{s}} V_{\mathbf{v}} \cdot U_{\mathbf{s}\mathbf{v}}. \tag{3}$$

The Gibbs thermodynamic potential for a condensed system can be found from (1):

$$G \simeq -kT \left[ \ln g \left( N_{\bar{\mathbf{D}}}, N_{\bar{\mathbf{T}}} \right) + \sum_{\bar{\mathbf{D}}} N_{\bar{\mathbf{D}}} \ln \psi_{\bar{\mathbf{D}}} = \frac{u \left( N_{\bar{\mathbf{D}}}, N_{\bar{\mathbf{T}}} \right)}{kT} \right]. \tag{4}$$

Since  $\tilde{U}(N_{\hat{D}}, N_{\hat{T}})$  is determined by the relationships (2) and (3), and  $\tilde{l}\tilde{n}\tilde{g}(N_{\hat{D}}, N_{\hat{T}})$  by formula [22]

$$\frac{\ln \hat{e}(N_{\hat{\mathbf{D}}}, N_{\hat{\mathbf{T}}})}{\ln \hat{e}(N_{\hat{\mathbf{D}}}, N_{\hat{\mathbf{D}}})} = \sum_{\hat{\mathbf{D}}} N_{\hat{\mathbf{D}}} \ln \frac{\hat{p}_{\hat{\mathbf{D}}}}{\hat{q}_{\hat{\mathbf{D}}}} = \sum_{\hat{\mathbf{D}}} \ln N_{\hat{\mathbf{D}}} + \frac{\sum_{\hat{\mathbf{D}}} (\hat{r}_{\hat{\mathbf{D}}} = \hat{q}_{\hat{\mathbf{D}}}) N_{\hat{\mathbf{D}}}}{\sum_{\hat{\mathbf{D}}} (\hat{r}_{\hat{\mathbf{D}}} = \hat{q}_{\hat{\mathbf{D}}}) N_{\hat{\mathbf{D}}}} \ln \left( \sum_{\hat{\mathbf{D}}} \hat{q}_{\hat{\mathbf{D}}} N_{\hat{\mathbf{D}}} \right) \ln \left( \sum_{\hat{\mathbf{D}}} \hat{r}_{\hat{\mathbf{D}}} \right) \ln$$

where  $\rho_{\tilde{D}}$  - number of methods of arrangement of the molecule on the quasi-lattice points of the solution in the case of the same fixed statistical segment,  $\sigma_{\tilde{D}}$  - coefficient of symmetry, r = number of statistical segments of the molecule, then the chemical potential of a particle of sort D is determined by the equation (cyclic structures of the associates and solvates are absent)

$$\mu_{\bar{\mathbf{D}}} = kT \left\{ -\ln \frac{\rho_{\mathbf{D}}}{q_{\mathbf{D}}} \psi_{\bar{\mathbf{D}}} + \ln N_{\mathbf{D}} - \frac{z}{2} q_{\bar{\mathbf{D}}} \ln \sum_{\bar{\mathbf{D}}} q_{\bar{\mathbf{D}}} N_{\bar{\mathbf{D}}} + r_{\bar{\mathbf{D}}} \left( \frac{z}{2} - 1 \right) \ln \sum_{\bar{\mathbf{D}}} r_{\mathbf{D}} N_{\bar{\mathbf{D}}} \right\} + \frac{z}{2} q_{\mathbf{D}} \sum_{\epsilon_{i}, \nu} U_{\epsilon_{i}, \nu} \left( V_{\epsilon}^{\mathbf{D}} V_{\nu} + V_{\nu}^{\mathbf{D}} V_{\epsilon} = V_{\epsilon} V_{\nu} \right).$$

$$(5)$$

Depending on the method of expression of the composition of the solution and the selection of the standard state of the component, expression (5) will acquire a different form. In the majority of works on extraction they use the molar concentrations as the method for expressing the composition of phases. Therefore, in this case there is sense in expressing the content of particles in the system in moles per liter, and as the standard state to select a solution which possesses the properties of an infinitely

diluted solution. Then the coefficient of activity of a particle of sort D can be calculated using the following formula:

$$\ln \gamma_{\rm D} = -\ln \frac{q_{\rm S} C_{\rm S}^{3}}{\sum_{\rm D} q_{\rm D} C_{\rm D}} = r_{\rm D} \left(\frac{z}{2} - 1\right) \ln \frac{q_{\rm S} \sum_{\rm D} r_{\rm D} C_{\rm D}}{r_{\rm S} \sum_{\rm D} q_{\rm D} C_{\rm D}} \div \left[r_{\rm D} \left(\frac{z}{2} - 1\right) + 1\right] \sum_{i,j} \frac{U_{z,j}}{kT} \left[V_{\bullet}^{\rm D} \left(V_{\bullet} - V_{\bullet}^{\rm S}\right) + V_{z}^{\rm D} \left(V_{\bullet} - V_{\bullet}^{\rm S}\right) - \left(V_{z} V_{\bullet} - V_{\bullet}^{\rm S} V_{\bullet}^{\rm S}\right)\right],$$

$$(6)$$

where  $c_{\widetilde{D}}$  - molar concentration of particles of sort  $\widetilde{D}$ , and the index S denotes the sort of particles which form the solvent.

Numerical appraisals using formula (6) are possible for specific systems and specific conditions of the experiment. Here we will consider only two important examples: a solution of monocctylphosphoric acid in  $\hat{\text{CCl}}_4$  and a solution of trioctylammonia nitrate in benzene.

Numerical appraisals. The system mono-N-octylphosphoric àcid (A) - complex (B) - CC .). Since an ion of the metal in its dimensions is considerably smaller than the dimensions of molecules of A and S, and the dimensions of A are approximately twice the dimensions of S, then  $r_{A} = r_{Mir} = 2r$  (r = degree of association of A) and  $r_{\bar{s}} = 1$ . Using expression (6), we obtain

$$\lg \frac{\gamma_{\text{Mir}}}{\gamma_r} = \left[2r\left(\frac{z}{2} - 1\right) + 1\right] \sum_{\epsilon_1, \nu} \frac{U_{\epsilon_1, \nu}}{2.3kT} \left[ (v_{\epsilon}^{\text{M}} - V_{\epsilon}^{\text{A}})(v_{\epsilon} - v_{\nu}^{\text{S}}) + \frac{1}{2} \left( V_{\epsilon}^{\text{M}} - V_{\epsilon}^{\text{A}} \right)(v_{\epsilon} - v_{\epsilon}^{\text{S}}) \right].$$

$$(7)$$

We will introduce specific designations for the classes of contact sectors: a - for actyl radicals, p - for phosphate groups, m - for phosphate groups in which at least part of the ions of hydrogen are replaced by the ions of metal, and s - for molecules of carbon tetrachloride. Then expressions (7) acquires the form

$$\lg \frac{\gamma_{\text{Mir}}}{\gamma_r} = i (z - 3) \frac{1}{2.3kT} \left[ V_a \left( U_{am} - U_{ap} \right) + \dot{V}_p \left( U_{pm} - U_{pp} \right) + V_{m} \left( U_{mm} - U_{mp} \right) + \left( V_s = 1 \right) \left( U_{ms} - U_{ps} \right) \right]. \tag{8}$$

It follows from formula (8) that the ratio of activity coefficients being considered in this case does not depend on r, but evidently depends on i = the number of particles M, entering into the composition of the given complex, which should be taken into account during summation.

For evaluating the interval of possible changes  $\frac{\gamma_{Mir}}{\gamma_r}$  we will use the following simplifications:  $U_{m\bar{s}} = U_{p\bar{s}} = U_{\bar{a}p} = \omega$  and  $U_{m\bar{m}} = U_{\bar{p}\bar{m}} = U_{\bar{p}\bar{p}}$ . The degree of polymerization of mono-N-octyl-phosphoric acid is great [24]. Therefore, instead of (8) we get

$$\lim_{N \to \infty} \frac{\gamma_{\text{Mir}}}{\gamma_r} = i \left( z - 3 \right) \frac{C_A}{\sum_{i=1}^{N} q_D C_D} \cdot \frac{\left( z - 3 \right) \omega}{2 \cdot 3 \cdot \hat{z} \cdot kT} \left( \varphi - 1 \right), \tag{9}$$

Where  $C_{A}$  = total concentration of A in the organic phase and

$$\varphi = \frac{U_{mm} - U_{pm}}{U_{ms} - U_{ps}}.$$

Evaluations of the variables, analogous to  $\omega$ , which were obtained in a number of works [25-30], showed that the value  $z \cdot \omega$  in modulus does not exceed 300 cal·mole<sup>-1</sup>. On the other hand, in the work of Tret'yakov and Rudakov [31] it was found that in the most diverse liquids, in which strong hydrogen bonds are absent, the free energy of intermolecular interactions lies in the interval from 3 to 5 kcal·mole<sup>-1</sup>. This interval answers to a change in from 0.6 to 1.7.

The results of calculations based on equation (9) with  $\omega=\pm\frac{300}{z}$ ,  $(\phi=1)=2.7$  and  $t=25^{\circ}C$  are given in Table 1.

It follows from the results of the calculations given in Table 1 that in an interpretation of experimental data based on the distribution of metals in extraction systems of the type being considered in a general case one cannot disregard the change in the ratio  $\gamma \text{Mir}/\gamma_r$  with a concentration of extracting reagent  $C_A > 1$  mole·1<sup>-1</sup> and with i > 1.

Tablé l Greatest possible values of the modulus of variable is for different coordination numbers of a quasi-lattice liquid

$\mathcal{O}_{c_{\Lambda}}$	Mogyns ig Mir npa i = 1				
(is M)	z ≅ 6	2 = 12	1=0		
0.01 0.05 0.1 0.5 1.0	0.0001 0.0007 0.0014 0.0070 0.0150	0.0003 0.0016 0.0032 0.0158 0.0324	0.0006 0.0028 0.0056 0.0280 0.0560		

Key: (1) 
$$C_A$$
 (in M); (2) Modulus of  $\log \frac{\gamma_{Mir}}{\gamma_r}$  when i=1.

The system nitrate of tri-N-octylamine (Å) - solvate (N) = benzene (S). During extraction of nitric acid by an amine salt a molecule of the nitric acid, by means of a hydrogen bond, is connected to a nitrate group of the amine salt, forming a solvate. Both the amine salt and the solvates apparently polymerized, although not to a strong degree [1]. A special feature of this system is that the dimensions of the molecules of nitric acid and benzene are close to each other. Consequently, the solvation of amine salt by nitric acid should be accompanied by growth of the statistical measurements of the particle. If r, just as previously, denotes the degree of polymerization of the amine salt or the solvate, then  $r_{Ar} = 5 \cdot r$ ,  $r_{Mir} = 5 \cdot r$  i and  $r_{s} = 1$ . The indices a, n and s denote the classes of the contact sectors belonging to the alkyl radical, the nitrate group and the molecule of benzene respectively. In this case equation (6) acquires the form

$$\begin{split} \lg \frac{\gamma_{\text{Mir.}}}{\gamma_r} &= \frac{i\left(z-2\right)}{2} \left\{ \lg \frac{\sum\limits_{\mathbf{D}} r_{\mathbf{D}} C_{\mathbf{D}}}{\sum\limits_{\mathbf{q}} q_{\mathbf{D}} C_{\mathbf{D}}} + \frac{2}{2(3kT)} \left[ \omega_{as} \left( V_a^2 + V_a V_a - V_a \right) + \right. \right. \\ &\left. + \omega_{as} \left( V_a^2 + V_a V_a - 2V_a - V_a \right) - \omega_{as} \left( V_a V_a - V_a \right) \right] \right\}. \end{split}$$

(10)

where 
$$v_{ij} = U_{ij} - \frac{1}{2}(U_{ii} + U_{jj})$$
.

Table 2 Greatest possible values of the modulus of  $\lg \frac{\tilde{I}_{MI\bar{I}}}{\tilde{I}_{\bar{I}}}$  for different concentrations of amine salt  $(\hat{C}_{A})$  and mitric acid  $(C_{M})$ ,  $t=25^{\circ}C$ 

<u>()</u>	MODANTE THE THE TENT TO THE TENT THE TE						
$c_{A}$	0.1 0.5 1.0			0.1	C <sub>M/C</sub> /	<u> </u>	
0.01 0.05 0.1 0.5 1.0	0.001 0.003 0.007 0.034 0.067	z = co 0.001		0.001 0.006 0.012 0.060 0.119	2 -> 8 0.001 0.006	0,m) 0,m 0,07 0,07; 0,15,	

Key: (1)  $\hat{C}_{A}$  (in M); (2) Modulus of  $lg \frac{\gamma_{Mir}}{\gamma_{r}}$ , when i=1.

Keeping in mind that the numerical evaluations are carried out for a concentration of reagent up to 1 mole  $1^{-1}$ , the following simplifications should be recognized as permissible:  $\tilde{V}_1\tilde{V}_1 \leqslant \tilde{V}_1$ ,  $\tilde{V}_1^2 \leqslant \tilde{V}_1$  and  $\tilde{v}_{uv} \simeq \tilde{v}_{uv}$ . From equation (10) we obtain

$$\lg \frac{\gamma_{\text{Mir}}}{\gamma_{r}} > \frac{i(z-2)}{2} \left[ \lg \frac{\sum_{\mathbf{D}} r_{\mathbf{D}} C_{\mathbf{D}}}{\sum_{\mathbf{D}} q_{\mathbf{D}} C_{\mathbf{D}}} - \frac{2\omega_{ns}}{2.3kT} (2\dot{V}_{n} + \dot{V}_{n}) \right]. \tag{11}$$

The results of the calculations using equation (11) are given in Table 2.

As it follows from the results of the calculations (Table 2), the need for taking into account the change in the coefficients of activity arises here at lower concentrations of reagent than in the case of extraction of metals by mono-N-octylphosphoric acid. Consequently, any model, intended for explaining data on the distribution of substances in systems with amine salts from the point of view of chemical events in the organic phase, cannot ignore this fact.

#### Conclusions

- A variant of a molecular-statistical model of an organic solution (extraction system) is proposed which includes associated reagents of the type of salts of alkylammonia and organophosphoric The statistico-thermodynamic equations take into account the contribution to the chemical potential of a particle in the mixture of the specific interactions, dimensions and symmetry of the particles, and also the change in the molecular force field of the medium with a change in the composition of the system.
- On the basis of equations obtained for the systems mono-N-octylphosphoric acid-complex-carbon tetrachloride and trioctylammonia salt-nitric acid-benzene numerical evaluations are given for the boundary concentrations where it is necessary to také into account the change in the coefficients of activity of the separate molecular individuals in the interpretation of data en distribution.

Submitted 8 Sep 1969

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